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**EUROPEAN PATENT APPLICATION**

21 Application number: 80103687.2

51 Int. Cl.<sup>3</sup>: **B 22 D 11/04**  
**B 22 D 11/06**

22 Date of filing: 30.06.80

30 Priority: 13.08.79 US 66254

43 Date of publication of application:  
11.03.81 Bulletin 81/10

84 Designated Contracting States:  
DE FR GB IT SE

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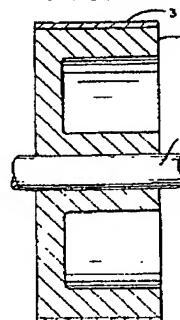
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54 **Apparatus and method for chill casting of metal strip employing a chromium chill surface.**

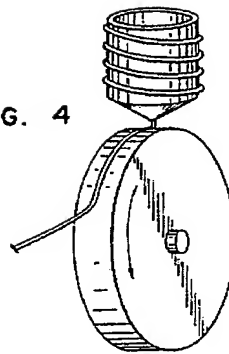
57 In the process of making metal strip directly from the melt by depositing molten metal onto the surface of a rapidly moving chill (1) body, the useful life of the surface of the chill body is prolonged, and strip properties are improved, by using a chill body (1) constructed of silver, copper or molybdenum, or alloys of silver, copper or molybdenum, having a chromium-coated chill surface (3) with critically defined thickness and surface texture.

**FIG. 1**



**EP 0 024 506 A1**

FIG. 4



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## DESCRIPTION

APPARATUS AND METHOD FOR  
CHILL CASTING OF METAL STRIP EMPLOYING A  
CHROMIUM CHILL SURFACEBACKGROUND OF THE INVENTION AND THE PRIOR ART

Methods are known for making continuous metal strip, of crystalline as well as amorphous (glassy) structure, directly from the melt by depositing molten metal onto the surface of a rapidly moving chill body whereon it is quenched to the solid state. The chill body may be a rotating wheel, cup or cyclinder, and the molten metal may be deposited onto the peripheral surface of the wheel or onto the inner surface of the cup or cyclinder. The chill body may also be a traveling belt, usually an endless belt. The metal may be deposited onto the surface of the chill body by methods such as jetting the molten metal onto the surface, moving the surface in contact with a meniscus or pendant drop of the molten metal to drag out a film of the metal, or by dipping the surface of the chill body into a bath of molten metal.

The surface of the chill body must meet several requirements. First, it must be wetted by the molten metal, or else formation of continuous strip will not take place. Second, it must be non-reactive with the molten metal, that is to say the molten metal must not attack, and must not weld to the chill surface, or else the strip cannot be cleanly separated therefrom. Third, it must have good thermal conductivity to permit rapid removal of heat as is necessary to effect rapid solidification of the molten metal to permit formation

of the molten metal, to permit formation of the glassy structure, and to optimize the properties of the metallic glass strip, especially to optimize its magnetic properties. Lastly, it must have sufficient wear resistance in continuous production of metal strip by the above-described quench casting process. Wear resistance is an extremely important aspect of chill body performance. High heat conductivity metals previously proposed to serve as chill body surface, such as copper, beryllium copper or silver, do not have the desired wear characteristics. Others, such as stainless steel, which would be expected to have good wear characteristics, fall short in other respects, such as failure to provide sufficient wetting, or good thermal conductivity.

#### SUMMARY OF THE INVENTION

In accordance with the present invention there is provided an improvement in the method for making metal strip directly from the melt by depositing the molten metal onto the surface of a rapidly moving chill body, which improvement comprises depositing the molten metal onto the surface of a chill body constructed of a metal selected from the group consisting of copper, silver, molybdenum and alloys thereof having a surface coating of chromium of thickness of from about 0.002 to about 0.15 millimeter, and having surface roughness of about 0.25 to about 3 micrometers.

The present invention further provides an improvement in the apparatus for making thin metal sections, such as splats or strip, directly from the melt by depositing the molten metal onto the surface of a rapidly moving chill body, which apparatus includes a chill body having a surface adapted to receive molten metal to be deposited thereon for rapid quenching together with means functionally connected with said chill body for depositing molten metal onto its surface, wherein the improvement comprises providing a chill body constructed of a metal selected from the group

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consisting of copper, silver, molybdenum and alloys thereof, having a surface coating of chromium of thickness of from about 0.002 to about 0.15 millimeter, and having surface roughness of about 0.25 to about 3 micrometers.

By the chill body being constructed of copper, silver, molybdenum or alloys thereof it is meant that these metals furnish the heat extracting member of the chill body, or the "heat sink", which absorbs the heat of the molten metal to effect rapid quenching thereof to the solid state, desirably at rates in the order of  $10^4 - 10^6$  °K/sec., or higher, as may be required for formation of metallic glass bodies from glass-forming alloy melts. This therefore does not mean that in the construction of the chill body other metals may not be employed, e.g. for structural purposes, such as reinforcement, and chill bodies incorporating other metals are intended to be within the scope of the appended claims.

I have surprisingly found that the above-described chromium surface coat, of the specified thickness and critically defined surface texture (surface roughness) is readily wetted by the molten metal, especially by iron, nickel and/or cobalt-based alloys which upon rapid quenching from the melt form amorphous structures (metallic glasses). Particularly good wetting seems to be obtained with glass-forming, iron-based, boron-containing metal melts wherein the metal component predominantly comprises iron. These are of considerable practical interest because of their outstanding soft magnetic properties, which make them eminently suitable for use in electromagnetic induction devices. The particular chromium surface further provides for good adhesion of the solidified metal strip, which is essential to effect thorough quenching of the metal if a ductile, amorphous metal strip is desired, yet it also affords clean release of the solidified strip from the surface. It is believed that

the surprising improvement in soft magnetic properties of iron-based, boron-containing metallic glasses quenched on the chill body of the present invention, which has been observed, is due to such good adhesion and thorough quenching.

Lastly, the particular chromium-coated chill bodies of the present invention combine the above-described advantageous wetting and quenching properties with excellent wear resistance.

The benefits of the above-described chill bodies having a chromium surface of specific thickness and surface structure in the process of making metal strip directly from the metal by depositing the molten metal onto the rapidly moving surface of a chill body are obtained regardless of the configuration of the chill body. That is to say, the chill body may be a rapidly rotating drum of which the exterior surface is used as the chill surface; it may be a rapidly rotating cylinder whereof the inner surface furnishes the chill surface, a moving belt, a cup-shaped structure, or any other structure. Further, any means of depositing the molten metal onto the chill surface, e.g. jetting, flowing, dragging, dipping and others may be employed, without restriction.

For purposes of the present invention, a strip is a slender body whose transverse dimensions are much less than its length. In that context, strips may be bodies such as ribbons, sheets or wires, of regular or irregular cross-section.

#### BRIEF DESCRIPTION OF THE DRAWINGS

The annexed drawings further illustrate the present invention.

Fig. 1 is a cross-sectional view of an annular chill roll, the exterior surface of which is coated with a chromium in accordance with the present invention;

Fig. 2 is a cross-sectional view of an annular chill roll having a ring of chromium-coated molybdenum

inserted in its surface.

Fig. 3 is a cross-sectional view of a cylindrical chill body having an inner chromium-coated chill surface inclined with respect to the axis of rotation;

5 Fig. 4 is a side view in partial cross-section showing means for jetting molten metal onto a rotating chill roll, and a rotating chill roll provided with a chromium-coated chill surface;

10 Fig. 5 is a somewhat simplified perspective view of apparatus including means for depositing molten metal onto a chill surface in the form of a moving endless belt having a chromium surface.

DETAILED DESCRIPTION OF THE INVENTION, OF THE PREFERRED EMBODIMENTS, AND OF THE BEST MODE PRESENTLY CONTEMPLATED  
15 FOR ITS PRACTICE

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Chill casting processes for making metal strip - polycrystalline as well as amorphous (glassy) metal strip - by depositing molten metal onto the surface of a rapidly moving chill surface of a heat  
20 extracting member (chill body) are well known. It has now been found that for use in such chill casting processes, chill bodies having heat extracting members of silver, copper, molybdenum or alloys thereof, which heat extracting members have a chromium-coated chill  
25 surface of very specific construction, have very desirable properties, especially for casting metallic glass strips of iron-based boron-containing alloys.

The chromium coating must be at least about 0.002 millimeter thick or else it is of little or no  
30 benefit, inter alia for the reason that it provides insufficient wear resistance. On the other hand, it may not be thicker than about 0.15 millimeters. I have found that substantially thicker chromium coatings result in insufficient quenching of the melt, and in  
35 general deterioration in physical properties of glassy metal strip cast thereon, especially loss in ductility and of magnetic properties, e.g. reduced maximum induction and permeability. Good results are obtained

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with chromium coatings having thickness of from about 0.01 to about 0.1 millimeter, more preferably of from about 0.01 to about 0.075 millimeter.

5       The second critical element is the surface  
texture of the chromium coat. It has been thought by  
those skilled in the metallic glass casting art that it  
would be difficult or impossible to cast metallic glass  
strip by quench casting techniques on chromium surfaces,  
principally because of their relatively low heat con-  
10       ductivity. Not only that, it was further found that  
such strip, when cast on a smooth chromium surface,  
even a smooth, thin chromium surface of thickness within  
the range of that contemplated by the present invention,  
fails to adequately wet the surface and to adhere to the  
15       surface sufficiently to obtain good quenching of the  
strip. Consequently, strip cast on smooth chromium  
surfaces tends to be brittle, to have non-uniform  
properties, and to lack good magnetic properties. Such  
strip is commercially unacceptable.

20       I have now surprisingly found that thin  
chromium coats having very specific surface texture  
avoid the above-described shortcomings, and instead  
provide for a high degree of heat transfer from the melt  
deposited onto the chill surface to the underlying heat  
25       sink to effect rapid solidification of the melt, and for  
a high degree of adherence of the solidified strip to  
the chill surface, to effect thorough and rapid  
quenching to below the crystallization temperature of  
the metal strip, thereby producing strip having good  
30       magnetic and physical properties. In order to obtain  
these desirable results, the surface roughness must be  
from about 0.25 to about 3.0 micrometers. Insufficient  
surface roughness below about 0.25 micrometers will  
tend to result in the above-described shortcomings of a  
35       smooth chromium surface. A higher degree of surface  
roughness above about 3.0 micrometers, while generally  
providing sufficient quench rate and adhesion, results  
in strip having undesirably high roughness on the



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surface cast in contact with the chill surface. Good results are obtained with chill surface texture corresponding to surface roughness of from 0.5 to about 2.0 micrometers, preferably of from about 0.6 to about 1.5 micrometers. The most preferred surface texture is a "satin finish", within the above-stated ranges of surface roughness, a satin finish being defined as a surface texture without visibly discernible lay, that is to say that surface roughness is the same measured in any direction. However, a satin finish, while providing the best results, is not absolutely necessary, and acceptable results are also obtained under conditions of discernible lay, such as where the finish runs longitudinal or transverse of the casting direction, or in any direction therebetween.

When amorphous metal strips are made by jetting molten glass forming alloy against the surface of a rapidly rotating chill body as, e.g., described in U.S. Pat. 4,077,462 to Bedell et al., or in U.S. Pat. 3,856,074 to Kavesh, the surface of the chill body becomes gradually eroded. A rough, uneven track is developed around the periphery of the chill body surface whereon casting of the strip takes place. Further casting into the same track produces strip of unacceptable quality, having a rough surface and ragged edges. The problem of chill surface wear in these processes is even more acute when casting takes place under vacuum. The absence of an intervening gas layer in vacuum casting allows a larger area of the chill surface to be impacted and wetted by the molten jet. Another factor which leads to severe wear on conventional chill surfaces is inclusion in the alloy being cast of appreciable amounts of refractory metals, e.g., molybdenum, tungsten, chromium, hafnium, iridium, niobium, osmium, platinum, rhenium, rhodium, ruthenium, tantalum, thorium, vanadium, and zirconium. Hence, use of the chill surface of the present invention is particularly advantageous when casting under vacuum

(say under absolute pressure of less than about 25 mm. Hg), or when casting glass-forming alloys containing one or more refractory metals, and especially when casting such alloys under vacuum.

5           The form of the chill body and the mode of the casting operation are not critical for purposes of the present invention. For example, casting may take place against the peripheral surface of a rapidly rotating drum by jetting molten metal against that surface, as  
10       disclosed in the above-mentioned patents to Bedell et al. and Kavesh. Casting may take place against the exterior surface of a rotating drum by drawing out the metal from a meniscus formed at a slotted nozzle, as described in U.S. Pat. 3,522,836 to King, or from a  
15       pendant, unconfined drop of molten metal as described in U.S. Pat. 3,896,203 to Maringer et al. Alternatively, the peripheral surface of the rotating chill drum may be dipped into a bath of molten metal as described in U.S. Pat. 3,861,450 to Mobley et al., or the molten metal may  
20       be deposited under pressure from a slotted nozzle onto the chill surface, as described in U.S. Pat. 4,142,571 to Narasimhan. Furthermore, the chill surface may be furnished by the interior surface of a rotating cylinder, as described in U.S. Pat. 3,881,540 to Kavesh  
25       and U.S. Pat. 3,881,542 to Polk et al., or as shown by Pond and Maddin in Trans. Met. Soc. AIME, 245 (1969) 2,475-6. Also, casting may take place into the nip two counter-rotating chill rolls, as for example described in U.S. Pat. 3,881,541 to Bedell, and by H.C. Chen and  
30       C.E. Miller, in Rev. Sci. Instrum. 41, 1237 (1970). Moreover, the chill surface may be furnished by the open concave surface of a rapidly rotating cup as disclosed in U.S. Pat. 2,825,108 to Pond; or a moving belt, desirably a moving endless belt, as described in U.S.  
35       Pat. 2,886,866 to Wade. The disclosures of the above-mentioned patents and publications are incorporated herein by reference. The advantages of the use of the specific chromium-coated chill body of the

present invention are obtained regardless of the construction of the chill body, and regardless of the means for depositing the molten metal onto the chill surface, that is to say whether by jetting, dragging  
5 from a meniscus or a pendant drop, forcing it through a slotted nozzle located in close proximity to the chill surface or by dipping into a bath of molten metal, or by any other suitable means.

The chromium coating or plating is suitably  
10 applied to the substrate of copper, silver, molybdenum or alloys thereof by means of electroplating, using conventional electroplating procedures, although other the procedures may be employed, if desired. Methods of chromium plating are well known, and generally involve  
15 passing a d.c. current through a suitable plating bath, e.g. one containing chromic acid together with a suitable "catalyst", typically sulfate ion provided by sulfuric acid, and using the surface to be plated as the cathode. The chromium plating operation can be  
20 facilitated, and the adhesion of the chromium coating can be improved by first applying to the surface to be plated a thin (e.g. less than about 0.01 millimeter thick) "strike" coat of nickel, as is conventional in chromium plating operation.

The surface texture, i.e. the above-described  
25 surface roughness, may be provided by treating the chill surface by suitable means before or after the chromium plating operation, or both before and after the chromium plating operation, with suitable abrasive. For  
30 ease of treatment, and to protect the integrity of the chromium coat, surface treatment before the chromium plating operation is preferred. Surface texture can suitably be obtained by abrading the chill surface with a suitable abrasive, such as emery cloth and the like,  
35 or by impinging a suitable finely divided hard powder against the chill surface, or by similar means. A very effective means involves "slurry honing", which involves impinging a fluid stream containing finely divided

suspended abrasive particles against the surface to be roughened.

In any event, methods of plating and of providing the specific surface texture are well known and are not part of the present invention.

When the chill body is to be made of molybdenum, it can be made by procedures usually employed for fabrication of molybdenum, including machining from solid stock, such as cast pieces, or fabrication by known powder metallurgical methods. A particularly desirable embodiment of the present invention is a composite chill body, especially a chill roll, made of copper provided with a hoop of molybdenum, as illustrated in Figs. 1 and 2. The casting surface provided by the molybdenum is chromium plated and has the above-described surface texture. With reference to Fig. 1, chill roll 1 made of copper is mounted for rotation on shaft 2. The exterior surface of chill roll 1 is provided with a hoop of molybdenum 3. In Fig. 1, the hoop of molybdenum covers the total peripheral surface of the chill roll. The molybdenum hoop may be affixed to the copper chill roll, e.g. by shrink fitting. Alternatively, a molybdenum surface may be provided by any other conventional surface coating method, as for example oxyacetylene spraying, a method which involves feeding a molybdenum wire into the cone of an oxygen/acetylene flame to melt the metal, and then propelling the molten metal in droplet form against the surface to be coated. Other suitable methods include plasma arc spraying and conventional cladding procedures.

Another embodiment of the present invention utilizing a copper-beryllium chill body from the conventional copper-beryllium alloys is also suitable.

Detailed design and construction of apparatus of the present invention is within the capability of any competent worker skilled in the art.

The following Example further illustrates the present invention and sets forth the best mode presently contemplated for its practice.

Example and Comparative Test

5           Apparatus employed was similar to that depicted in Fig. 4 employing a water-cooled copper chill roll having a 0.025 millimeter thick satin finish chromium coating with surface roughness of about .76 - .80 micrometers (about 30-34  $\mu$  inch). The chill roll had a  
10   diameter of 38.1 cm (15 inch), and it was rotated at a speed to provide peripheral velocity of from 914 to 1067 meter/min (3000-3500 ft/min). The nozzle for depositing the molten metal had an orifice of 2.54 cm (1 inch) length and 0.5 mm (20 mil) width. The gap between the  
15   chill surface and the nozzle was about 0.25 mm (about 10 mil). Alloy of composition  $\text{Fe}_{81}\text{B}_{13.5}\text{Si}_{3.5}\text{C}_2$  (atom percent) was ejected through the nozzle into contact with the rotating chill surface under pressure at the rate of about 4.53 kg./min. (10 lbs/min). It  
20   solidified on the surface of the chill roll into a strip 2.54 cm (1 inch) wide and about 0.038 cm (1.5 mil) thick.

          A comparative run employing a copper chill roll without the above-described chromium coating, but  
25   under otherwise identical conditions, was made. Properties of the strip obtained in the Example and in the comparative run are summarized in the Table, below.

          It was noted that the chromium coated chill roll did not show any discernible wear after 110 kg of  
30   metal had been cast in 12 consecutive runs of about equal size, each on the same "track". A plain copper wheel would show considerable wear after a single run, and the chill surface would require "dressing" after each individual run to restore the chill surface to the  
35   necessary degree of smoothness required to make strip of acceptable surface characteristics.

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TABLE

Magnetic Properties of Cast Strip  
(data shown for beginning and end of Run)

		<u>Comparative Run</u>	<u>Example</u>
5	<u>As Cast</u>		
	Coercivity $H_c$ (Oe)	0.11/0.18	0.055/0.078
	Remanence $B_{(0)}$ (k Gauss)	5.2/4.3	7.2/6.8
	Saturation Induction		
	at $10^{-3}$ Oe $B_{(1)}$ (k Gauss)	6.7/5.6	8.0/7.8
10	Permeability $\times 10^{-3}$	29/16	100/70
	Core Loss (W/lb) <sup>(1)</sup>	0.69/0.78	0.65/0.56
	(2)		
	VA Demand (V /lb)	37.8/43.2	21.7/16.7
	<u>Field Annealed (3)</u>		
	Coercivity $H_c$ (Oe)	0.11/0.11	0.04/0.045
15	Remanence $B_{(0)}$ (k Gauss)	8.0/2.6	13.8/12.5
	Sat. Induction $B_{(1)}$ (k Gauss)	12.8/8.0	15.0/14.6
	Permeability $M_{max} \times 10^{-3}$	75/15	333/218
	Core Loss (W/lb)	0.11/0.32	0.079/0.072
	VA Demand V/lb)	0.98/18.4	0.145/0.184
20	(1) Loss of watts/lb of core in transformer.		
	(2) Volts-Amperes in driving coil of transformer required to bring core to operating magnetization.		
	(3) Obtained on a toroid annealed as follows:		
25	Temperature	365°C	
	Time at Temperature:	2 hrs.	
	Atmosphere:	dry argon	
	Magnetizing Field:	10 Oe, circumferential	
	Cooling rate to 100°:	about 15°C/min.	

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As the data in the Table demonstrate, the strip cast on the chromium plated surface having specific surface texture has substantially improved magnetic properties as compared to strip cast in conventional manner on a copper chill surface. Differences in magnetic properties from beginning to the end of the run are substantially less in each instance. Transformers made from strip cast on such chromium plated chill roll will have substantially improved efficiency, in that they will have greatly reduced core losses, and greatly reduced VA demand.

Since various changes and modifications may be made in the invention without departing from the scope and essential characteristics thereof, it is intended that all matter contained in the above description shall be interpreted as illustrative only, the invention being limited only by the scope of the appended claims.

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I claim:

1. A method for making metal strip directly from the melt by depositing the molten metal onto the surface of a rapidly moving chill body, characterized in  
5 that the molten metal is deposited onto the surface of chill body having a heat-extracting metal selected from the group consisting of copper, silver, molybdenum and alloys thereof and having a surface coating of chromium of thickness of from about 0.002 to about 0.15  
10 millimeter, and having surface roughness of from about 0.25 to about 3.0 micrometers.

2. The method of claim 1 wherein the chill body is a chill roll and the molten metal is deposited into its peripheral surface and wherein the metal  
15 is one which, upon rapid quenching from the melt, forms an amorphous (glassy) body.

3. The method of claim 1 wherein the chill body is an endless belt constructed of copper-beryllium alloy.

20 4. Apparatus for making thin metal sections directly from the melt by depositing molten metal onto the surface of a rapidly moving chill body comprising a chill body having a surface adapted to receive molten metal to be deposited thereon for rapid quenching  
25 together with means functionally connected with said chill body for depositing molten metal onto its surface, characterized in that the chill body is constructed of a metal selected from the group consisting of copper, silver, molybdenum and alloys thereof, having a surface  
30 coating of chromium of thickness of from about 0.002 to about 0.15 millimeter, and having surface roughness of about 0.25 to about 3 micrometers.

5. The apparatus of claim 4 wherein the surface coating has a satin finish without discernible lay.

35 6. The apparatus of claim 5 wherein the chill body is a chill roll.



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7. The apparatus of claim 6 wherein the chill roll is constructed of copper-beryllium alloy.

8. The apparatus of claim 6 wherein the chill roll is constructed of molybdenum.

9. The apparatus of claim 7 wherein the chill  
5 body is an endless belt.

10. The apparatus of claim 9 wherein the endless belt is constructed of copper-beryllium alloy.

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FIG. 1

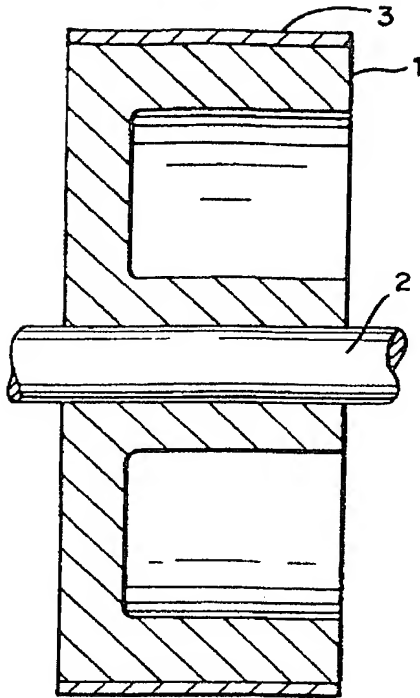


FIG. 2

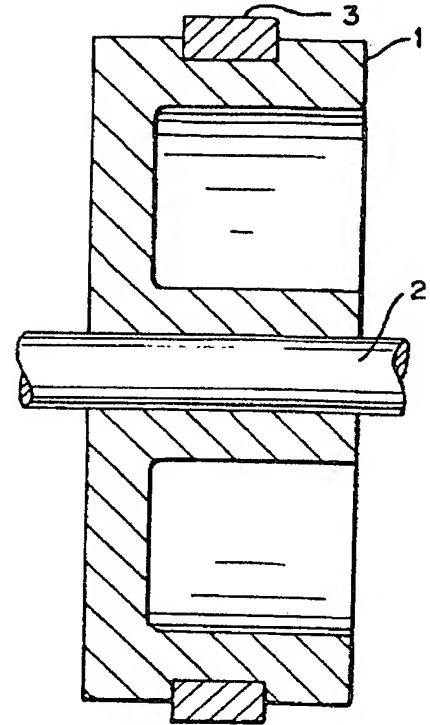
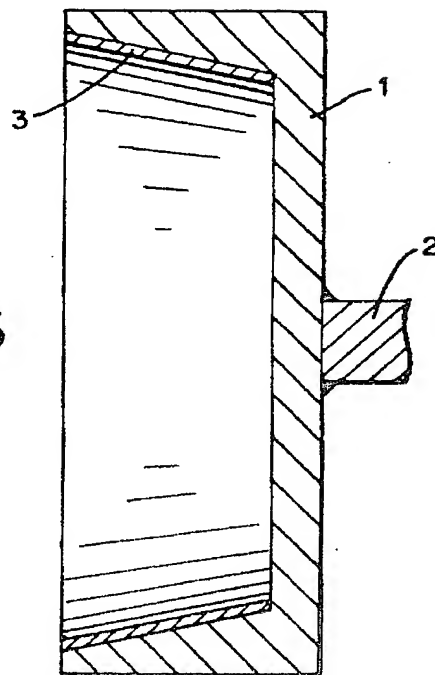


FIG. 3



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FIG. 4

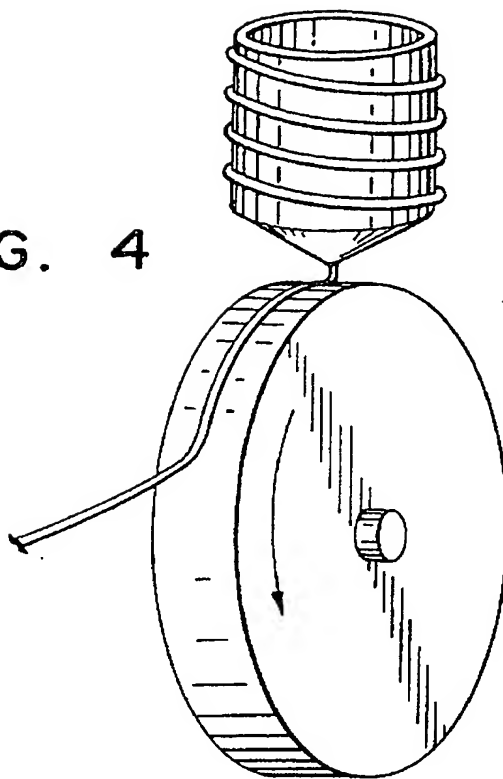
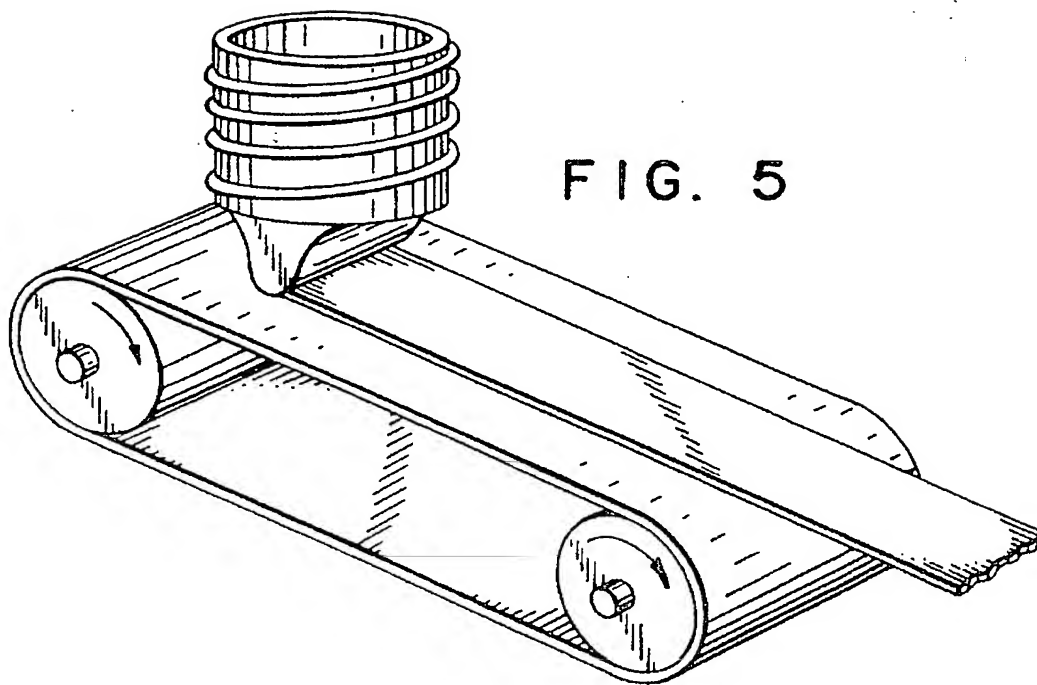


FIG. 5





European Patent  
Office

# EUROPEAN SEARCH REPORT

0024506

Application number

EP 80 10 3687.2

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl.)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
X	<u>DE - C - 814 925</u> (WIELAND-WERKE AG) * claims 1 and 2 * -- <u>DE - C - 969 000</u> (GEBR. BÖHLER & CO.) * claim 1 * --	1  1	B 22 D 11/04 B 22 D 11/06
A	<u>DE - B1 - 2 842 421</u> (VACUUMSCHMELZE) * claim 9 * --	1	TECHNICAL FIELDS SEARCHED (Int. Cl.)
A	<u>DE - A - 1 508 975</u> (SCHLOEMANN AG) * claims 6,7 and 8 * --	1,4,7	B 22 D 11/00
A	<u>DE - A1 - 2 701 636</u> (KABEL- & METALL- WERKE) * claim 6 * --	10	
A	<u>DE - A1 - 2 837 432</u> (SONY CORP.) * claim 15 * --	1	
A	<u>DE - A1 - 2 838 296</u> (MISHIMA KOSAN CO.) * claim 1; page 2, lines 1 to 10 * ----	1	CATEGORY OF CITED DOCUMENTS
X The present search report has been drawn up for all claims			X: particularly relevant A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention E: conflicting application D: document cited in the application L: citation for other reasons
			&: member of the same patent family, corresponding document
Place of search Berlin		Date of completion of the search 20-11-1980	Examiner GOLDSCHMIDT